

Chemistry

Lecture 4

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Alcohols, Phenols, Ethers

Outline:

Alcohols:

- ✚ Classification
- ✚ Nomenclature
- ✚ Reactivity

Phenols:

- ✚ Physical properties
- ✚ Nomenclature
- ✚ Acidity
- ✚ Reactivity

Alcohols

- General formula is $C_nH_{2n+2}O$ or $C_nH_{2n+1}OH$

Types:

- ◆ **Monohydric Alcohols:** Alcohols having only one $-OH$ group
- ◆ **Dihydric Alcohols:** Alcohols having two $-OH$ group
- ◆ **Polyhydric Alcohols:** Alcohols having more than two $-OH$ group

Types of Monohydric Alcohols:

- ◆ **Primary Alcohols:** If carbon to which $-OH$ group is attached is further directly attached with one or no carbon atom.
- ◆ **Secondary Alcohols:** If carbon to which $-OH$ group is attached is further directly attached with two carbon atoms.
- ◆ **Tertiary Alcohols:** If carbon to which $-OH$ group is attached is further directly attached with three carbon atoms.

Common Names of Alcohols:

- ◆ Alkyl alcohol
like CH_3OH is methyl alcohol, C_2H_5OH is called ethyl alcohol

IUPAC Rules for Alcohols:

Selection of Chain:

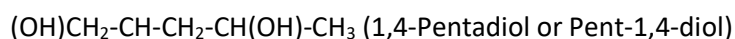
- ✿ Select the longest continuous carbon chain to –OH group is attached directly.
- ✿ If more than one chain is of same length, then select one with maximum no. of –OH groups.
- ✿ If no. –OH groups is same, select one with maximum substituents and if substituents are also same, then select any.

Numbering:

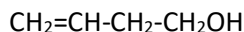
- ✿ Start numbering from the end nearer to –OH group and if –OH group is at same distance from both ends, start numbering from end nearer to substituent.
- ✿ If substituent is also at same distance, then start numbering from either end.

Naming:

- ✿ Name alkane is replaced with “alkanol”.
Position of substituent-name of substituent-position of OH group-alkanol
- ✿ If more than one -OH groups are present, use diol, triol, tetraol etc.

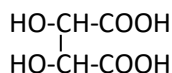


- ◆ In case of unsaturated alcohols, -OH group is preferred over double or triple bonds.

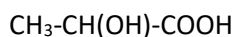


3-Buten-1-ol or But-3-en-1-ol

- ◆ If more than functional groups are present, preference is with one coming first in priority list i.e.



2,3-Dihydroxy butane-1,4-dioic acid (Tartaric acid)



2-Hydroxy propanoic acid (Lactic acid)

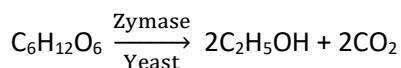
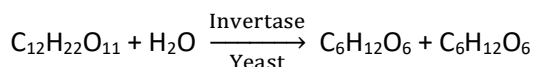
Preparation of Ethanol

- ◆ By Fermentation (a biochemical process occurs in presence of enzymes)
- ◆ Necessary condition are:
 - ❖ Optimum temperature (25-35°C)
 - ❖ Proper aeration
 - ❖ Dilution of solution
 - ❖ Absence of any preservative
- ◆ In Pakistan prepared from **molasses, starch, grains, and fruit juices**.

From Molasses:

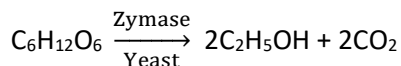
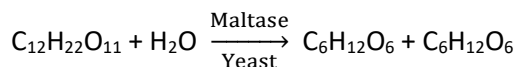
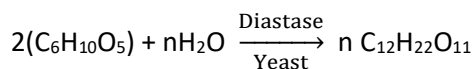
- Residue after crystallization of sugar from sugar juice

- So it is sucrose
- Sucrose on hydrolysis in presence of Invertase breaks into glucose and fructose
- Glucose further decomposes in presence of Zymase to give ethanol



From Starch:

- Starch on hydrolysis in presence of Diastase breaks into maltose
- Maltose on hydrolysis in presence of Maltase breaks into glucose units
- Glucose further decomposes in presence of Zymase to give ethanol



- ◆ Ethanol never exceeds 12-14 % as beyond this limit enzyme becomes inactive
- ◆ Distillation gives Rectified spirit (95 %)
- ◆ Distillation in presence of CaO gives Absolute alcohol (100 %)
- ◆ 10 % methanol is added in ethanol to avoid its drinking (denaturing)
- ◆ Pyridine or acetone can be used

Reactions of Alcohol

| 1. When O-H bond is to be broken | 2. When C-O bond is to be broken |
|---|--|
| Act as nucleophile except as acid with only Na | Act as electrophile |
| Attack of electrophile on it | Attack of nucleophile on it |
| Show electrophilic substitution reactions except with Na gives acid base reaction | Show nucleophilic substitution reactions |
| Reactivity/Acidity; Methyl alcohol > 1° > 2° > 3° | Reactivity; 3° > 2° > 1° > Methyl alcohol |
| $2\text{C}_2\text{H}_5\text{OH} + 2\text{Na} \xrightarrow{\text{Ether}} 2\text{C}_2\text{H}_5\text{ONa} + \text{H}_2$ | $\text{C}_2\text{H}_5\text{OH} + \text{SOCl}_2 \xrightarrow{\text{Pyridine}} \text{C}_2\text{H}_5\text{Cl} + \text{SO}_2 + \text{HCl}$ |
| $\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{MgI} \xrightarrow{\text{ZnCl}_2} \text{CH}_4 + \text{Mg(I)(OC}_2\text{H}_5)$ | $\text{C}_2\text{H}_5\text{OH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{C}_2\text{H}_5\text{Cl} + \text{H}_2\text{O}$ |
| $\text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{COOH} \xrightleftharpoons{\text{H}_2\text{SO}_4} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ | $\text{C}_2\text{H}_5\text{OH} + \text{NH}_3 \xrightarrow{\text{ThO}_2} \text{C}_2\text{H}_5\text{NH}_2 + \text{H}_2\text{O}$ $\text{C}_2\text{H}_5\text{OH} + \text{PCl}_3 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{H}_3\text{PO}_3$ $\text{C}_2\text{H}_5\text{OH} + \text{PCl}_5 \rightarrow \text{C}_2\text{H}_5\text{Cl} + \text{POCl}_3 + \text{HCl}$ |

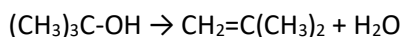
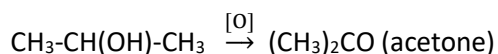
The rate of esterification of alcohol is more for?
 $\text{C}_2\text{H}_5\text{OH}$ CH_3OH $(\text{CH}_3)_2\text{CHOH}$ $(\text{CH}_3)_3\text{COH}$

3. Oxidation Reactions:

- $\text{KMnO}_4/\text{H}_2\text{SO}_4 \Rightarrow$ Pink colour of KMnO_4 disappears
- $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4 \Rightarrow$ Colour turns green due to reduction of dichromate ion (Cr^{+6}) to chromate ion (Cr^{+3})
- Primary alcohols on oxidation give aldehydes which in same conditions further oxidize to carboxylic acids.
- Secondary alcohols on oxidation give ketones which do not oxidize further in such conditions
- Tertiary alcohols don't oxidize rather undergo elimination reaction to give alkene

Which of the following alcohol not undergo oxidation?

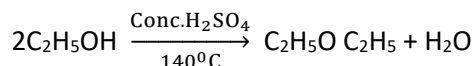
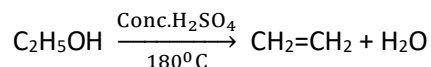
ethanol propanol iso-butanol
2-methyl-2-propanol



Oxidation of iso-propyl alcohol yields?

propane propanone propanal
propanoic acid

4. Dehydration:



The dehydration of alcohol results in:
alkene aldehyde ether both a, c

5. Lucas Test:

- Alcohols form oily layer of respective alkyl halide with HCl in presence of ZnCl_2
- Primary alcohols form oily layer on heating
- Secondary alcohols form oily layer in 5-10 min.
- Tertiary alcohols form oily layer immediately

6. Iodoform Test (I_2/NaOH):

What happens when iodine is treated with methyl alcohol in presence of base?
Oily layer forms yellow ppt form no reaction

- Yellow ppts. of iodoform (CHI_3) forms
- Only ethanol gives iodoform test among primary alcohols
- Those secondary alcohols give iodoform test in which at least one $-\text{CH}_3$ group is attached with α -carbon
- Tertiary alcohols don't give iodoform test

Uses of Methanol

- Methanol is used as a solvent for fats oils, paints, and varnishes.
- It is also used as antifreeze in the radiators of automobiles
- For denaturing of alcohol.

Uses of Ethanol

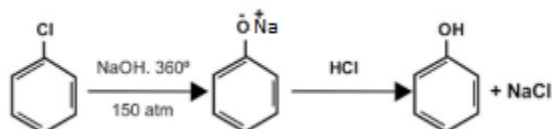
- Ethanol is used as a solvent, as a drink and as a fuel in some countries.
- It is used in pharmaceutical preparations
- As a preservative for biological specimen.

Phenol

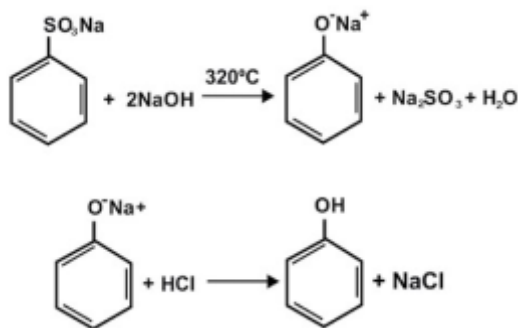
- Carboic acid
- Obtained from coal tar by Runge
- Deliquescent
- Anesthetic
- Sparingly soluble in water at room temp. giving pink solution.
- Poisonous with characteristic phenolic order
- Used to prepare pharmaceutical drugs
- As disinfectant in hospitals and washrooms
- More acidic than alcohol and water due to stability of phenoxide ion
- Phenoxide ion has 5 resonating structures (reason for stability)
- Acidity order **Carboxylic acid > Phenol > Water > Alcohol**

Preparation of Phenol

➤ From Chlorobenzene (Dow's method)



➤ From sodium salt of benzene sulphonic acid



Reactions of Phenol

(a) Involving Benzene Ring:

◆ With Br₂:

- Test to distinguish phenol from rest



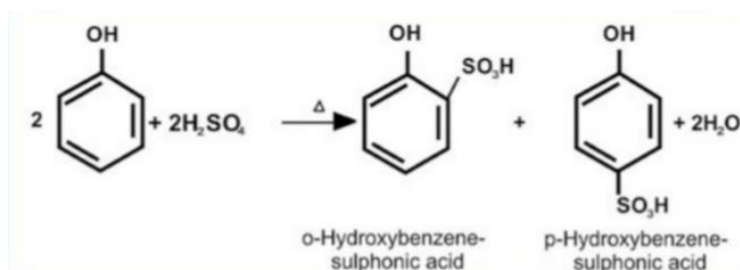
- White ppts. of 2,4,6-Tribromophenol

◆ **Nitration:**



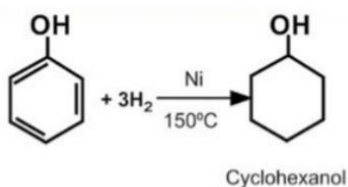
◆ **Sulphonation:**

- Phenol reacts with conc. H_2SO_4 to form ortho, para hydroxy benzene sulphonic acid.



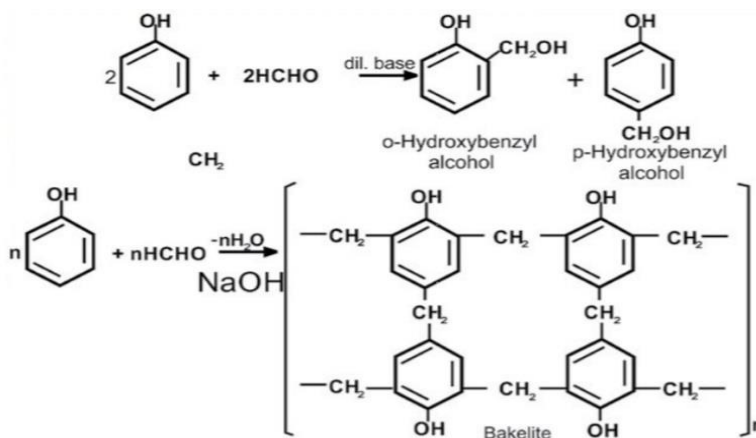
◆ **Hydrogenation:**

- On hydrogenation, phenol gives cyclohexanol



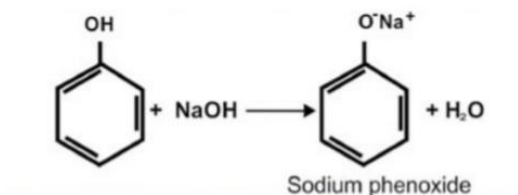
◆ **Reaction with Formaldehyde:**

- Phenol + formaldehyde in presence of alkali/acid produce ortho, para hydroxyl benzyl alcohol
- This hydroxyl benzyl alcohol further react with phenol molecule to form Bakelite (polymer).

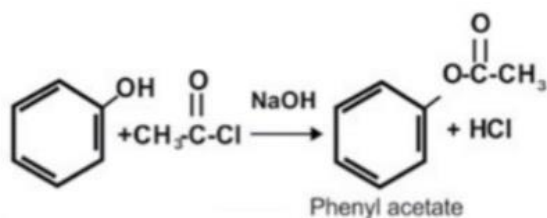


(b) Involving –OH group:

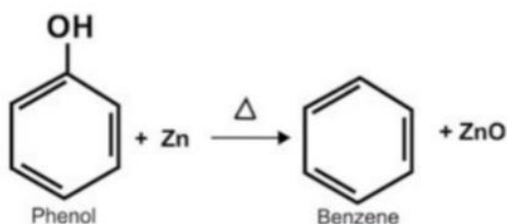
- ◆ **Salt Formation:** Phenol reacts with alkalies to form salts



- ◆ **Ester Formation:** Phenol reacts with acetyl chloride in presence of base to form ester



- ◆ **Reduction with Zn:** Phenol reduces with Zn to give benzene



Ethers

Common Names of Ethers:

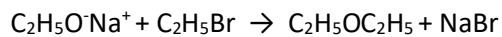
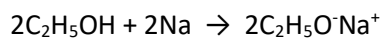
- ⚙ If **R** groups are same, use di as prefix i.e. CH₃-O-CH₃ is Dimethyl ether.
- ⚙ If **R** groups are different, name them alphabetically i.e. C₂H₅-O-CH₃ is Ethyl methyl ether.

IUPAC Names of Ethers:

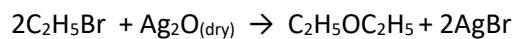
- ⚙ If **R** groups are different, name the smaller **R** group as "**alkoxy**" while the larger group as parent name "**alkane**".
- ⚙ If **R** groups are different, name the any of them as "**alkoxy**" while the other one as parent name "**alkane**".

Preparation of Ethers

(a) Williamson synthesis



(b)



Reactivity

- Comparatively inert
- Behave as lewis base

